

HYDROUS PYROLYSIS OF n -C₃₂H₆₆ IN THE PRESENCE AND ABSENCE OF INORGANIC COMPONENTS

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Keywords : hydrocarbon cracking, n -alkanes, n -alkenes, n -alkanones

Introduction

There has been much research on catagenetic processes by laboratory simulations. These experiments are performed over short durations but at elevated temperatures to compensate for the lower temperature organic reactions which occur over geologic timescales. Experimental designs for achieving these reactions have been quite diverse. In addition to varying time and temperature, many different combinations of experimental parameters have been used including: vacuum or controlled atmosphere conditions, open or closed systems, different reaction vessel materials, aqueous or anhydrous conditions, varied mineral assemblages, and a wide range of organic source materials (e.g., 1-7). Hydrous pyrolysis is a closed system procedure of heating a sample which is submerged in water and not in contact with water vapor or supercritical water (8). It appears to be the most promising system since it most closely mimics the conditions found in nature, especially those found in hydrothermal systems (9). In this paper, the study of the aqueous high temperature organic chemistry of n -C₃₂H₆₆ in the presence or absence of several selected inorganic components is presented. The experiments were performed under nitrogen in a stainless steel reaction vessel, the only variable being the addition of inorganic species. The results of these experiments are relevant for hydrous pyrolysis studies of sedimentary source materials where large amounts of inorganic salts and minerals are present.

Experimental

A 250 mL stainless steel vessel (Parr Instrument T316SS) used for the reactions was equipped with a thermocouple for temperature control ($\pm 2^\circ\text{C}$) and a gage block assembly for recovery of volatiles. Conditioning of the vessel prior to each experiment was done by heating it with 63.5 mL water at 350°C for 24 h. No effort was made to remove air from the system during the conditioning process. The experiments are summarized in Table 1. For each experiment 0.050 g of n -C₃₂H₆₆ and 63.5 mL of deoxygenated water alone or water and an equimolar amount of inorganic species were combined in the reaction vessel. The deoxygenated water was prepared by bubbling N₂ gas into distilled water for twenty minutes before each experiment. Assembly of the reaction vessel was done in a glove bag under a nitrogen atmosphere. The vessel was then placed in a heater and temperature maintained at 350°C for 72 h. In the case of the H₂O - n -C₃₂H₆₆ - sulfide system, the interior of the vessel was coated with a sulfide formed by heating the vessel with 0.5 g elemental sulfur and 63.5 mL water for 24 h. After cooling to room temperature, the excess sulfur was rinsed from the vessel leaving a uniform sulfide coating. Then under a N₂ atmosphere, 0.050 g of n -C₃₂H₆₆ and 63.5 mL of deoxygenated water were combined and allowed to react.

The vessel was cooled to room temperature before opening and contents transferred to a separatory funnel. The interior of the vessel was rinsed with methanol and methylene chloride, which were added to the separatory funnel, and the organic fraction was separated. The water was extracted with two additional 20 mL portions of methylene chloride. The organic fractions were combined and concentrated.

The products were fractionated by thin layer chromatography (20 x 20 cm, 250 microns Silica Gel G) into four fractions using heptane as developer. Hydrogenation of selected

samples was done by bubbling H_2 gas into the sample for 30 minutes in the presence of platinum (IV) oxide (Adams' catalyst).

Gas chromatography (GC) was performed using a Hewlett-Packard 5890 gas chromatograph equipped with a DB-5 open tubular column (30 m x 0.25 mm ID, 0.25 μ m film) programmed from 65° (isothermal 2 min.) to 310°C at 4°C/min. (isothermal 30 min.). Compound identification was aided by comparison with authentic standards.

Results

Although a large amount of cracking occurred, there was no gas pressure in any of the heating experiments. Most of the unreacted starting material along with the cracking products was in the form of a wax disk floating on the water. The walls of the vessel were also coated with the wax which made it difficult to ensure that all of the organic material was completely transferred from the vessel for analysis.

The GC traces of the total extracts are shown in Fig. 1. They are characterized by a broad distribution of cracking products with a large amount of unreacted starting material. The cracking products range in carbon number from C_9 to C_{31} . The cracking products in all experiments maximized at C_{16} , half the carbon number of the starting material. The total extracts consisted primarily of a nonpolar fraction of n -alkanes and n -alkenes and a polar fraction made up of oxygenated compounds. A low amount of branched and aromatic compounds were formed under these conditions.

H_2O - n - $C_{32}H_{66}$. Chromatograms of the nonpolar fraction before and after catalytic hydrogenation confirms the presence of the n -alkene isomers (Fig. 2a and 2b). The n -alkanes were the major products of hydrocarbons with 16 or more carbon atoms. No particular series dominated in hydrocarbons less than C_{16} . The polar fraction consisted of homologous n -alkanal and n -alkan-2-one series in addition to other oxygenated species (Fig. 2c).

H_2O - n - $C_{32}H_{66}$ - NaCl. The nonpolar and polar fractions were similar to the H_2O - n - $C_{32}H_{66}$ system but the n -alkane predominance of the heavier hydrocarbons was not observed.

H_2O - n - $C_{32}H_{66}$ - HCl. The acidic conditions favored the formation of n -alkanes over n -alkenes. No significant differences in the polar fraction was observed.

H_2O - n - $C_{32}H_{66}$ - NaOH. A simple product distribution was generated which was composed primarily of terminal n -alkenes with a minor amount of n -alkanes. A similar distribution of polar compounds was generated in this experiment.

H_2O - n - $C_{32}H_{66}$ - NH_4Cl . The formation of n -alkanes over n -alkenes was slightly favored in this system when compared to the H_2O - n - $C_{32}H_{66}$ system but a similar distribution of polar compounds were formed.

H_2O - n - $C_{32}H_{66}$ - Na_2SO_4 . Cracking products below C_{14} were low in this experiment. The nonpolar fraction consisted mainly of n -alkanes and terminal n -alkenes in approximately equal amounts for each carbon number.

H_2O - n - $C_{32}H_{66}$ - Elemental Sulfur. The formation of n -alkanes was favored by the addition of elemental sulfur. The n -alkan-2-ones were present but formed in lower amounts.

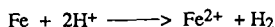
H_2O - n - $C_{32}H_{66}$ - Sulfide. This system greatly favored the formation of n -alkanes over any other products, and n -alkan-2-ones were the major series in the polar fraction (Fig. 3).

Discussion

These preliminary experiments were designed to study the effects that some selected inorganic components have on the aqueous pyrolysis of a representative n -alkane. The choice of systems was not comprehensive but does include some major components likely to be found when experimenting with sediments and whole rocks.

Hydrous pyrolysis of n - $C_{32}H_{66}$ results in the formation of alkanes, alkenes, and to a lesser extent oxygenated species. Relative amounts of the products were affected by the inorganic species present in the system. The formation of n -alkene isomers by these pyrolysis experiments confirms the results previously described where terminal n -alkenes and a range of internal n -alkenes, formed by double bond migration, were produced during aqueous pyrolysis of n -hexadecane at 317°C (10). Acid-catalyzed double bond migration was also observed in

the aqueous pyrolysis of 1-decene to form 2-, 3-, 4- and 5-decene (11). The low hydrogen ion concentration under alkaline conditions ($\text{H}_2\text{O} - n\text{-C}_{32}\text{H}_{66} - \text{NaOH}$) did not permit much double bond migration. This lack of secondary double bond migration resulted in terminal n -alkenes as the major products, preserving the original cracking products formed by the homolytic bond cleavage of $n\text{-C}_{32}\text{H}_{66}$. The increase in the hydrogen ion concentration in the NH_4Cl and HCl systems favored a higher alkane to alkene ratio relative to the $\text{H}_2\text{O} - n\text{-C}_{32}\text{H}_{66}$ system, indicating an enhancement of hydrogenation occurred under acid conditions. This result may be due to the interaction with the stainless steel vessel to alter the hydrogenation capacity of the reaction system. The corrosion of the stainless steel reaction vessel by the following reaction has been proposed to account for a change in pH observed in some experiments (12) :



The increased hydrogen ion concentration in the acidic systems could drive this reaction to the right, producing a larger amount of hydrogen gas. This could provide the increased hydrogenation capacity necessary to result in the observed increases in the alkane to alkene ratios. The alkaline conditions of the NaOH system resulted in a greatly diminished hydrogenation capacity to produce a low alkane to alkene ratio. The role of the initial oxidation state of the sulfur species can be seen by comparing the sulfate, elemental sulfur and sulfide systems. The distribution of n -alkanes and terminal n -alkenes as primary products of the $\text{H}_2\text{O} - n\text{-C}_{32}\text{H}_{66} - \text{Na}_2\text{SO}_4$ system suggests that aqueous sulfate consumes hydrogen ions to decrease both the acid-catalyzed double bond isomerization and the hydrogenation capacity of the system, resulting in a nonpolar fraction similar to the alkaline $\text{H}_2\text{O} - n\text{-C}_{32}\text{H}_{66} - \text{NaOH}$ system. Both elemental sulfur and sulfide generate acidic systems but the lack of n -alkenes indicates a strongly hydrogenating system. The polar fraction of the sulfide system consisted mainly of n -alkan-2-ones. The n -alkan-2-ones are one of several series of polar compounds commonly found in oils collected from interiors of high temperature hydrothermal vents of the Guaymas Basin hydrothermal system (13). The results of these laboratory experiments suggest that these oxygenated compounds may be formed entirely by thermogenic processes.

Conclusions

The products generated by the heating experiments appear to be the result of primary cracking of $n\text{-C}_{32}\text{H}_{66}$ to form alkenes followed by secondary reactions of these cracking products. The main findings are listed below :

1. Primary cracking of $n\text{-C}_{32}\text{H}_{66}$ produced a homologous series of terminal n -alkenes.
2. Specific acid-catalyzed double bond isomerization of the terminal alkenes occurred where a sufficient hydrogen ion concentration existed.
3. The extent of alkene hydrogenation was affected by the hydrogen ion concentration, possibly by corrosion of the stainless steel reaction vessel.
4. The initial oxidation state of sulfur had a major effect on controlling the product distribution, with elemental sulfur and sulfide favoring n -alkane generation.

These experiments provide information on how some inorganic species influence the predominant chemical reactions which n -paraffins undergo under high temperature aqueous conditions. These preliminary results suggest that care should be taken when comparing the results from simple aqueous pyrolysis systems to whole rock and whole sediment pyrolyses where the mineral and salt contents are vastly different.

Acknowledgements

We thank the National Science Foundation, Division of Ocean Sciences (Grant OCE-9002366), the Donors of the Petroleum Research Fund administered by the American Chemical Society and the Gilbert Fellowship Program of the U. S. Geological Survey, for support of this research.

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Table 1. Summary of reaction systems performed in 63.5 mL H₂O at 350°C for 72 h.

Figure	System Description	Reactant Amounts
1a	H ₂ O - n-C ₃₂ H ₆₆	0.050 g n-C ₃₂ H ₆₆
1b	H ₂ O - n-C ₃₂ H ₆₆ - NaCl	0.050 g n-C ₃₂ H ₆₆ 0.111 mmol NaCl
1c	H ₂ O - n-C ₃₂ H ₆₆ - HCl	0.050 g n-C ₃₂ H ₆₆ 0.111 mmol HCl
1d	H ₂ O - n-C ₃₂ H ₆₆ - NaOH	0.050 g n-C ₃₂ H ₆₆ 0.111 mmol NaOH
1e	H ₂ O - n-C ₃₂ H ₆₆ - NH ₄ Cl	0.050 g n-C ₃₂ H ₆₆ 0.111 mmol NH ₄ Cl
1f	H ₂ O - n-C ₃₂ H ₆₆ - Na ₂ SO ₄	0.050 g n-C ₃₂ H ₆₆ 0.111 mmol Na ₂ SO ₄
1g	H ₂ O - n-C ₃₂ H ₆₆ - Sulfur	0.050 g n-C ₃₂ H ₆₆ 0.111 mmol Sulfur
1h	H ₂ O - n-C ₃₂ H ₆₆ - Sulfide	0.050 g n-C ₃₂ H ₆₆ Sulfide coated vessel

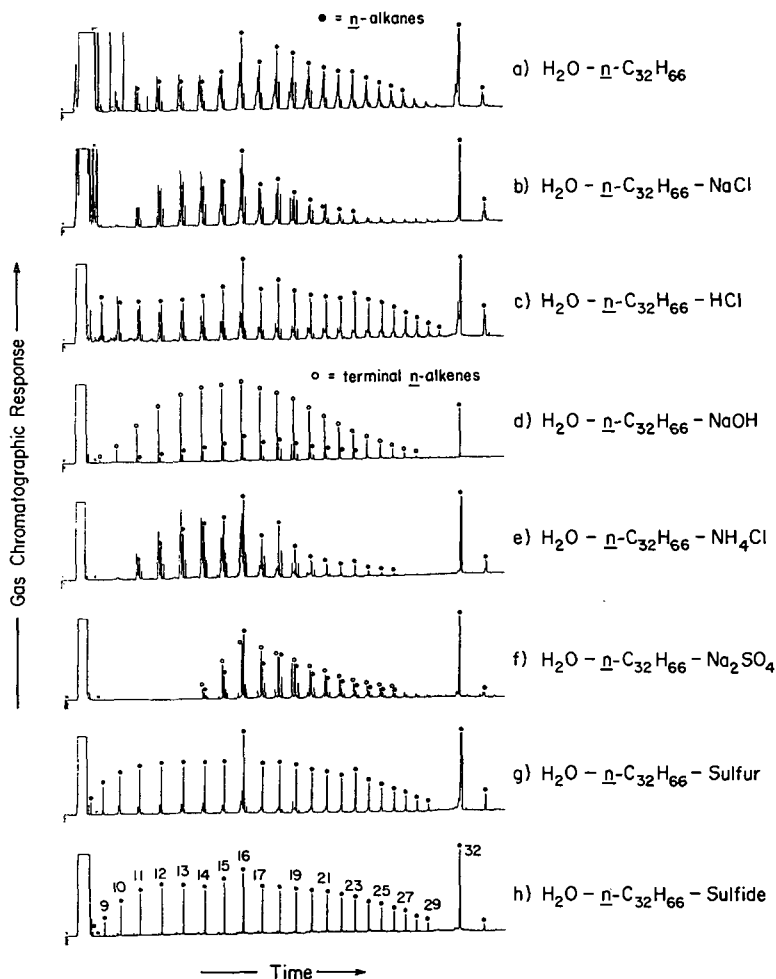


Fig. 1. Gas chromatograms of the total extracts from the hydrous pyrolysis experiments : a) $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66}$; b) $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66} - \text{NaCl}$; c) $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66} - \text{HCl}$; d) $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66} - \text{NaOH}$; e) $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66} - \text{NH}_4\text{Cl}$; f) $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66} - \text{Na}_2\text{SO}_4$; g) $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66} - \text{Sulfur}$; h) $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66} - \text{Sulfide}$. [GC conditions : oven was temperature programmed from 65° (isothermal 2 min.) to 310°C at $4^\circ\text{C}/\text{min}$. (isothermal 30 min.)]. Numbers refer to carbon chain lengths of the n-alkanes .

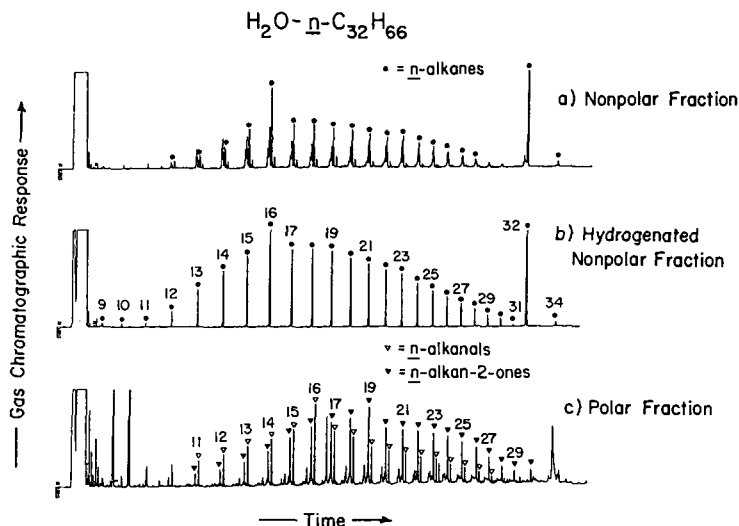


Fig. 2. Gas chromatograms of the $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66}$ system : a) nonpolar fraction before catalytic hydrogenation; b) nonpolar fraction after catalytic hydrogenation; c) polar fraction. Numbers refer to carbon chain lengths.

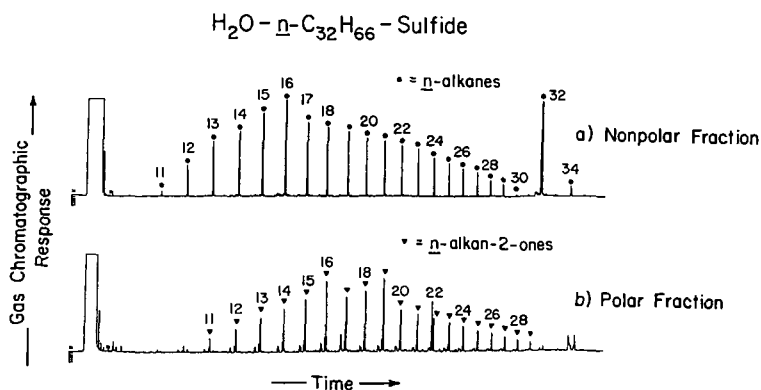


Fig. 3. Gas chromatograms of the $\text{H}_2\text{O} - \text{n-C}_{32}\text{H}_{66} - \text{Sulfide}$ system : a) nonpolar fraction; b) polar fraction. Numbers refer to carbon chain lengths.